Crystal structure of 1,1′-methylenedipyridinium dibromide monohydrate, $(C_{11}H_{12}N_2)Br_2 \cdot H_2O$

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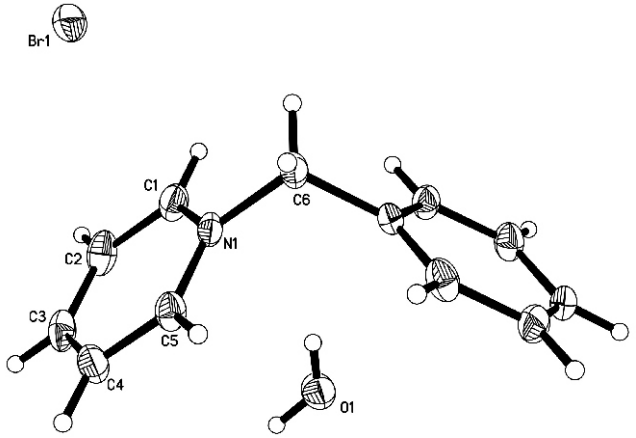

Abstract

$C_{11}H_{14}Br_2N_2O$, orthorhombic, *Fdd*2 (no. 43), a = 19.364(3) Å, b = 16.814(2) Å, c = 8.1486(9) Å, V = 2653.1 Å^3, Z = 8, $R_{gt}(F)$ = 0.025, $wR_{ref}(F^2)$ = 0.061, T = 295 K.

Source of material

A mixture of pyridine (0.1 mol) and dibromomethane (0.05 mol) was reacted under nitrogen atmosphere with stirring at 353 K for 48 h. The resulting clear solution was evaporated under vacuum. Colourless crystals suitable for X-ray analysis were obtained by slow evaporation of a water solution over a period of three weeks (yield 73 %). Elemental analysis — found: C, 37.75 %; H, 4.04 %; N, 8.02 %. calculated for $C_{11}H_{14}Br_2N_2O$: C, 37.74 %; H, 4.03 %; N, 8.00 %.

Experimental details

All H atoms on C were placed at idealized positions and refined as riding on their parent atoms with d(C—H) = 0.93 Å, U_{iso}(H) = 1.2 U_{eq}(C), d(O—H) = 0.85 Å, U_{iso}(H) = 1.5 U_{eq}(O). One of the hydrogen atoms attached to the oxygen atom O1 of the water molecule (H1B) was located at general position with S.O.F of 0.5, i.e. half-occupied. The Flack parameter is 0.00(2).

Discussion

N-Heterocyclic carbene ligands (NHC) have been shown to have wide applicability in coordination chemistry and catalysis [1]. The preparation of chelating bis(NHC) ligands is also receiving much attention, since they can provide additional air and moisture stability for the metal centers [2]. Morever, this class of compounds represents a class of ammonium salts that are excellent directing regents for the construction of metal-organic architectures [3].

The title crystal structure consists of 1,1'-methylenedipyridinium cations and bromide anions. A two-fold rotation axis passes through the methylene carbon atom of the dication (∠N–C–N = 110.96(2)°). The water molecule also lies on a two-fold rotation axis. The bond length d(C6—N1) = 1.464(4) Å, and the bond angle ∠N1–C5–C4 = 120.65(3)° are similar to the reported methylenedipyridinium dichloride monohydrate [4]. In the crystal, the cations are stacked along [010] forming channels that are occupied by the bromide anions. Adjacent molecules are connected into a two-dimensional network through O–H···Br, O–H···N hydrogen interactions.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.25 × 0.32 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	60.93 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	55.46°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10484, 1281
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1177
$N(param)_{refined}$:	75
Program:	SHELXTL [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1)	16*b*		0.2057	0.3880	0.2407	0.049
H(2)	16*b*		0.2578	0.4844	0.3987	0.055
H(3)	16*b*		0.3653	0.4639	0.5052	0.050
H(4)	16*b*		0.4234	0.3465	0.4461	0.050
H(5)	16*b*		0.3694	0.2508	0.2919	0.042
H(6A)	16*b*	0.50	0.2844	0.2254	0.0827	0.050
H(6B)	16*b*	0.50	0.2156	0.2746	0.0827	0.050
H(1A)	8*a*		¼	¼	0.4938	0.071
H(1B)	16*b*	0.50	0.2689	0.2818	0.6656	0.071

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	16*b*	0.2829(1)	0.3109(1)	0.2544(3)	0.033(1)	0.027(1)	0.031(1)	–0.0092(9)	0.0045(9)	0.0009(9)
C(1)	16*b*	0.2495(2)	0.3795(2)	0.2837(5)	0.032(1)	0.032(2)	0.059(2)	–0.000(1)	0.001(2)	0.012(1)
C(2)	16*b*	0.2808(2)	0.4369(1)	0.3777(6)	0.049(2)	0.023(1)	0.066(2)	0.001(1)	0.017(2)	–0.004(2)
C(3)	16*b*	0.3446(2)	0.4251(2)	0.4401(4)	0.051(2)	0.031(1)	0.044(2)	–0.015(1)	0.009(1)	–0.007(1)
C(4)	16*b*	0.3790(2)	0.3550(2)	0.4063(5)	0.033(1)	0.038(1)	0.055(2)	–0.007(1)	–0.004(1)	–0.001(1)
C(5)	16*b*	0.3469(1)	0.2984(2)	0.3140(4)	0.032(1)	0.024(1)	0.049(2)	0.001(1)	0.003(1)	–0.003(1)
C(6)	8*a*	¼	¼	0.1526(5)	0.055(2)	0.042(2)	0.028(2)	–0.025(2)	0	0
Br(1)	16*b*	0.32445(2)	0.37541(1)	–0.1361(1)	0.0401(2)	0.0297(2)	0.0396(2)	–0.00493(9)	–0.0034(1)	–0.0026(1)
O(1)	8*a*	¼	¼	0.5981(4)	0.049(2)	0.054(2)	0.039(2)	–0.013(1)	0	0

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